Optical properties of ZrZn2 from 0.6 to 3.8 eV

Heide, P.A.M. van der; Baelde, W.; Groot, R.A. de; Vroomen, A.R. de; Mattocks, P.G.

Published in:
Journal of Physics F%3A Metal Physics

DOI:
10.1088/0305-4608/14/7/021

Publication date:
1984

J. Phys. F: Met. Phys. **14** (1984) 1745–1750. Printed in Great Britain

Optical properties of $ZrZn_2$ from 0.6 to 3.8 eV

P A M van der Heide, W Baelde, R A de Groot, A R de Vroomen and P G Mattocks†

Research Institute for Materials, Faculty of the Sciences, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Received 26 September 1983, in final form 9 December 1983

Abstract. In this paper we report ellipsometry measurements on $ZrZn_2$ at room temperature under ultra-high vacuum conditions. The optical constants have been determined in the energy range 0.6–3.8 eV. The results are compared with calculated optical conductivity curves based on the recent band-structure calculation of de Groot *et al*. Peaks in the experimental optical conductivity at 0.92, 1.22 and 3.02 eV could be assigned to direct transitions, in agreement with the band model.

1. Introduction

There has been considerable interest in the compound $ZrZn_2$ in recent decades. This interest stems primarily from the fact that $ZrZn_2$ shows ferromagnetism at low temperatures although it is made from 'non-magnetic' elements. Enz and Matthias (1978, 1979) revitalised the interest in this compound by suggesting the possibility of finding p-state pairing superconductivity if the magnetism could be suppressed.

In order to explain the physical properties of $ZrZn_2$ two groups performed band-structure calculations (Jarlborg *et al* 1981, de Groot *et al* 1980). The results of these calculations were in close agreement with each other. A good test of the reliability of band-structure calculations at the Fermi energy is provided by de Haas–van Alphen measurements. De Haas–van Alphen measurements on $ZrZn_2$ performed by van Ruitenbeek *et al* (1982) were in close agreement with the band-structure model. Optical experiments can, however, provide information on the bands at energies away from E_F. Photoemission measurements can give direct information about the band structure, but because of experimental problems in obtaining a $ZrZn_2$ crystal with a clean and stoichiometric surface, no photoemission experiments on $ZrZn_2$ have been reported previously. Ellipsometry measurements are somewhat less demanding in terms of sample-surface composition because of the much longer penetration depth of 1–4 eV photons compared with the escape length of the electrons in photoemission measurements (although care should still be taken).

The optical constants of $ZrZn_2$ reported by Veal *et al* (1971) were measured by means of reflectivity on a wrinkled foil and obtained by Kramers–Kronig analyses. These data were compared with an early band-structure calculation on $ZrZn_2$ in which the zinc atoms were neglected (Koelling *et al* 1971).

The advantage of ellipsometry measurements is that they provide the optical constants

† Department of Physics, State University of New York, Buffalo, New York, USA

0305-4608/84/071745 + 06 $02.25

directly without relying on Kramers–Kronig analyses which—in principle—can only be performed exactly if measurements over the entire spectroscopic range are available.

2. Method

2.1. Experiment

The optical constants of $ZrZn_2$ were measured by means of photometric ellipsometry.

The basic set-up is the one used by Castelijns *et al* (1975) and Castelijns (1977). Linearly polarised monochromatic light is incident on the sample and after reflection the light is polarised elliptically. Measurement of the resulting intensity of the light for different analyser positions gives the information required to calculate the parameters $\tan\psi$ and $\cos\Delta$ (Beattie 1955) from which the dielectric constants ε_1 and ε_2 can be determined. From the values of ε_2 obtained the optical conductivity and the joint density of states (JDOS) can be calculated. The relation between ε_2 and these two quantities is given by

$$\text{JDOS} = A \sum_{i,f} \int_{*} \mathrm{d}k\, \delta(E_f(k) - E_i(k) - \hbar\omega) = \omega^2 \varepsilon_2 \tag{1}$$

$$\sigma = \omega \varepsilon_2 . \tag{2}$$

where i and f denote initial and final states and $\hbar\omega$ the photon energy used.

In the past year several improvements have been made to the equipment, the most important being the addition of a microprocessor which now controls the measurements fully and transmits measured data on-line to an IBM 4341 computer, where further data reduction is done. It also allowed us to develop a new alignment method and also makes a much better error calculation possible.

Our equipment can be used from 0.6–6.0 eV; however, for the measurements described in this paper usable intensities were only available from 0.6–3.8 eV due to the smallness of the sample.

Light from a quartz halogen lamp or a xenon arc lamp is passed through a monochromator. Glan–Thompson prisms or Glan prisms were used as polarisers depending on the energy range used. The resulting linearly polarised, monochromatic light is incident on the sample at an angle of roughly 70°.

The reflected light is passed through an analyser, identical to the polariser, and the resulting intensity of the light for different analyser settings is measured with a photomultiplier or a PbS cell depending on the energy range used.

The reproducibility of the polariser and analyser settings is approximately 0.03°. Measurements were taken with an energy spacing of 0.03 eV; only in the strongly structured low-energy region were steps of 0.01 eV or less used.

At a given energy, for two polariser settings φ_p, at $+45°$ and $-45°$ with respect to the plane of incidence, the intensity after reflection is measured for eight analyser settings φ_A 45° apart. From these 16 measured intensities

$$I = I_0(n) F(\delta\varphi_A + \tfrac{1}{4}m\pi, \delta\varphi_p + \tfrac{1}{4}n\pi, \tan\psi, \cos\Delta) \tag{3}$$

with $m = 1$–8 and $n = 1$ and -1, four values for the ellipsometric parameters $\tan\psi$ and $\cos\Delta$ can be calculated using the formulae given by Beattie (1955). In formula (3) $\delta\varphi_A(\delta\varphi_p)$ are the deviations of the analyser (polariser) positions from the true values of $\varphi_A(\varphi_p)$.

From the resulting values of $\tan\psi$ and $\cos\Delta$ and the statistical error on these values

the dielectric constants ε_1 and ε_2, the JDOS (using the constant matrix element approximation), the optical conductivity, reflectivity and dielectric loss function and the errors in these derived quantities can be calculated and plotted routinely.

The $ZrZn_2$ sample used was grown as described by Mattocks and Dixon (1981). An area of 2×1 mm^2 of the crystal could be used for ellipsometry. Laue photographs of the sample indicated that it consists of two or three single crystals. It was polished using successively finer powders, finishing with 1 μm diamond powder. This resulted in a shiny surface of which 95% was perfect while the remainder had some scratches of the order of 0.5 μm and some pits of depth 8 μm. Immediately after polishing the sample was rinsed with pure alcohol and was introduced into an ion-getter pumped vacuum system in which the measurements were performed at a pressure of 2×10^{-9} Torr.

Because $ZrZn_2$ has a cubic crystal structure (C15) the dielectric constants can be calculated using the formulae for isotropic samples (Born and Wolf 1959). The values of ε_1 and ε_2 are plotted in figure 1. The errors in the measured values are a few per cent. Some small structures can be seen in the graph of ε_2.

The JDOS, optical conductivity, dielectric loss function and reflectivity were also derived from the experimental data. No evidence for bulk or surface plasmons was found. The observed structure was the most clear in the optical conductivity, which is given in figure 2. A curve, which is also shown in figure 2, was fitted to the measured points using the least-squares method. For three parts of the spectrum, i.e. from 0.6–1.1 eV, from 1.1–1.6 eV and from 2.4–3.6 eV, a good fit was obtained by fitting a Lorentzian on a parabolic background through each peak. Three peaks are clearly observable at 0.92, 1.22 and 3.02 eV. The error in the positions is 0.03 eV.

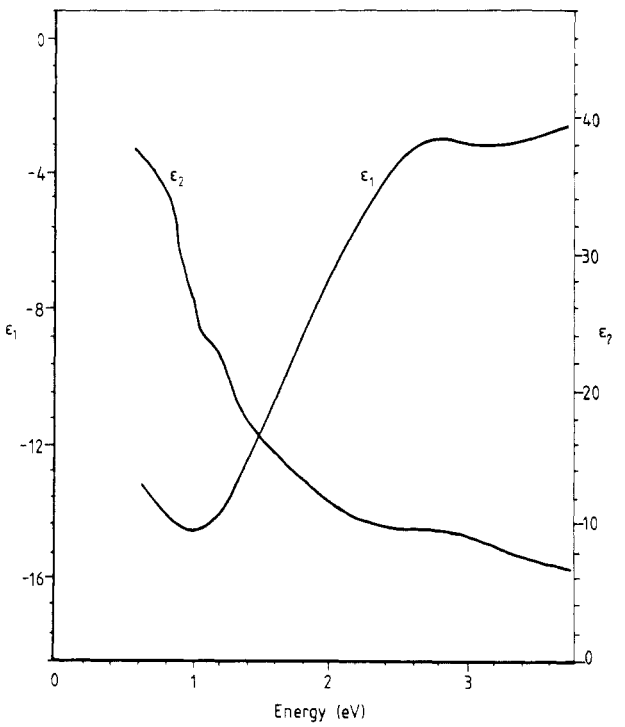

Figure 1. The real part of the dielectric constant ε_1 and the imaginary part of the dielectric constant ε_2 from the measured data.

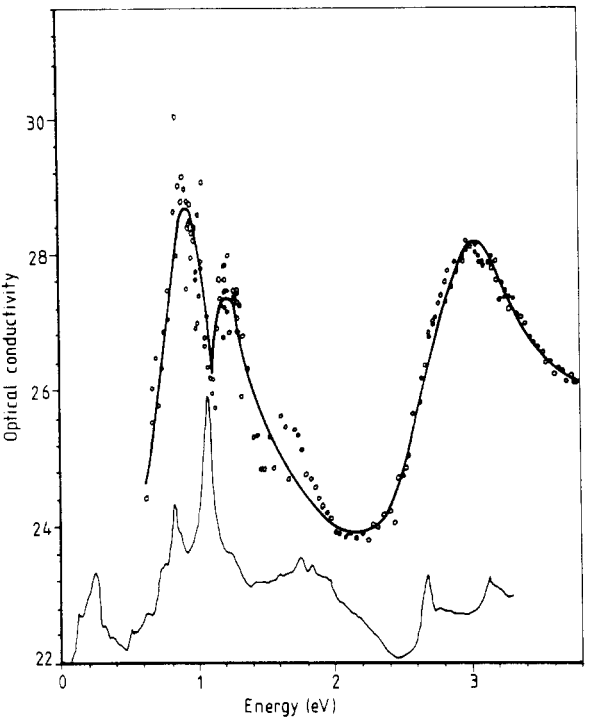

Figure 2. The optical conductivity of $ZrZn_2$ from the experimental data (heavy full curve) and from the calculation (in arbitrary units; thin full curve).

It was not possible to subtract a free-electron contribution (Drude term) from the measured data; to do this measurements at energies lower than 0.6 eV are necessary.

2.2. Theory

The optical conductivity was calculated from the band structure (de Groot *et al* 1980). The band structure along high-symmetry lines is shown in figure 3. There are 20 Zn d bands below the bottom of the panel. Bands 21 and 22 are mainly of Zn-type s, p character. The character of bands 23 and 24 shows strong dispersion, being of primarily Zr-type d character at L and also for band 24 at Γ. Elsewhere these bands are of mixed s, p character, centred on the Zr as well as the Zn sites. The wavefunctions of bands 25 and 26 also have a strong k dependence. At Γ and W the Zr-centred d character is the most important. At K and L the bands hybridise strongly, while at X the s, p character is dominant. Bands 27–30 are mainly Zr-centred d bands with various amounts of hybridisation.

The calculation of the optical conductivity requires the knowledge of the eigenvalue spectrum at many k points. A direct first-principles calculation at so many k points is prohibitively expensive. In order to circumvent this problem the ten lowest APW value bands (21–30) at 89 k points were fitted to a Fourier series containing 44 stars. The error in the fit for the worst case was 41 meV and the RMS error was about 14 meV. In the Brillouin zone integration $\frac{1}{24}$th of the zone was divided into 2000 cubes. The eigenvalues at the corners of these cubes were obtained from the Fourier fit. Eigenvalues within a cube were obtained by Lagrange interpolation; 4000 random points per cube were used. In this

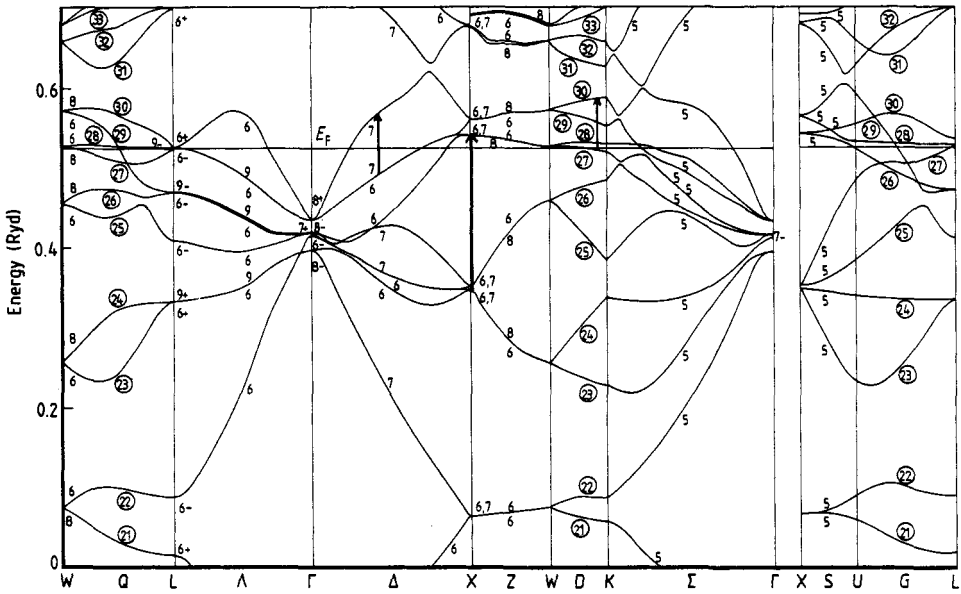

Figure 3. The band structure of $ZrZn_2$ along high-symmetry lines (de Groot *et al* 1980). Three transitions are marked at 0.83, 1.08 and 2.68 eV. The band numbers are circled; other numbers designate representations.

way 8×10^6 semi-random points in $\frac{1}{24}$th of the Brillouin zone were used. The matrix elements were considered to be constant in this calculation.

The calculated optical conductivity is also given in figure 2. It shows four clear peaks at 0.28, 0.83, 1.08 and 2.68 eV. The peak at 0.28 eV falls outside the spectroscopic range of our ellipsometer and will not be considered here. The program locates the points in the Brillouin zone where $E_n(k) - E_m(k)$ is an extremum; from these we know where and between which bands the transitions corresponding to the peaks in the optical conductivity find their main contributions. The peak at 0.83 eV stems from transitions between band 27 and band 30 at the edge of the zone near the D line (between W and K) but not exactly on it. The peak at 1.08 eV is caused by transitions between bands 28, 29 and 30 around the middle of the line. Transitions between initial bands 25 and 26 and final-state bands 27 and 28 are responsible for the peak at 2.68 eV. There may also be a contribution from excitations from bands 25 and 26 to bands 31 and 32 around W at this excitation energy. These transitions are located around the point X in the Brillouin zone. These points are indicated by arrows in figure 3.

3. Discussion

The experimental optical conductivity shows primarily three peaks at 0.92, 1.22 and 3.02 eV. The peak positions agree fairly well with the calculated peaks at 0.83, 1.08 and 2.68 eV. The peak heights are rather different, however. The peak at 1.08 eV is calculated to be the strongest peak, while the measured peak at 1.22 eV is somewhat weaker than the other two. This discrepancy is without doubt due to our neglect of matrix elements in the calculation of the optical conductivity.

Our experimental results are not in agreement with the values found by Veal *et al*

(1971), which no doubt can be attributed to their sample quality (a wrinkled foil of $ZrZn_2$) and their experimental method which had to use the Kramers–Kronig relations. Their theoretical optical conductivity, calculated neglecting the zinc atoms, also shows peaks at 0.9 and 2.7 eV. For other energies there is no agreement with our results, as could be expected because of the relative simplicity of their model.

Let us consider the peak positions in more detail. The band-structure calculation gave results in close agreement with DHVA data. In this calculation the muffin-tin approximation within the muffin-tin spheres was used. Corrections to the muffin-tin form of the potential are expected to be small in this compound (de Groot and Janner 1984). Moreover, in the isoelectronic isostructural compound $TiBe_2$ the non-muffin-tin corrections could be deduced from DHVA experiments (van Ruitenbeek *et al* 1984), and were found to be small (87 meV). Moreover, non-muffin-tin corrections will not influence the transition at 1.08 eV and will influence the transitions at 0.83 and 2.68 eV only slightly. Comparison between the experimental and theoretical peak positions shows that the calculated peak positions are consistently too small by about 10%. Relaxation effects accompanying optical excitations are expected to be important if the degree of localisation of initial and final states is different (Williams *et al* 1975). Since this is not the case here, we do not expect these effects to play a major role. It is well known that the local density approximation leads to empty states consistently too low in energy. We conclude that the discrepancy between the calculated and experimental peak positions is probably due to the local density approximation.

Acknowledgments

The authors would like to acknowledge the assistance of L Schreurs and H Weijers in the preparation of the $ZrZn_2$ sample for the ellipsometry experiment. We also thank J van Huet for constructing the microprocessor controller.

One of us (RdG) would like to acknowledge the support by the research program of the 'Stichting voor Fundamenteel Onderzoek der Materie' with financial support from the 'Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek'.

References

Beattie J R 1955 *Phil. Mag.* **46** 235

Born M and Wolf E 1959 *Principles of Optics* (Oxford: Pergamon)

Castelijns J H P 1977 *Thesis* University of Nijmegen

Castelijns J H P, Derks J P C M and de Vroomen A R 1975 *J. Phys. F: Met. Phys.* **5** 2407–14

Enz C P and Matthias B D 1978 *Science* **201** 828–9

—— 1979 *Z. Phys.* B **33** 129–33

de Groot R A and Janner A G M 1984 to be published

de Groot R A, Koelling D D and Mueller F M 1980 *J. Phys. F: Met. Phys.* **10** L235–40

Jarlborg T, Freeman A J and Koelling D D 1981 *J. Magn. Magn. Mater.* **23** 291–8

Koelling D D, Johnson D L, Kirkpatrick S and Mueller F M 1971 *Solid State Commun.* **9** 2039

Mattocks P G and Dixon A E 1981 *J. Phys. F: Met. Phys.* **11** L147–52

van Ruitenbeek J M, van Deursen A P J, Schreurs L W M, de Groot R A, de Vroomen A R, Fisk Z and Smith J L 1984 *J. Phys. F: Met. Phys.* to be published

van Ruitenbeek J M, Verhoef W A, Mattocks P G, Dixon A E, van Deursen A P J and de Vroomen A R 1982 *J. Phys. F: Met. Phys.* **12** 2919–28

Veal B, Mueller F M, Afshar R and Shaffer J 1971 *Proc. 17th Annual Conf. on Magnetism and Magnetic Materials*

Williams A R, de Groot R A and Sommers C B 1975 *J. Chem. Phys.* **63** 628–31